

# Statistical Physics

Objective is to understand macroscopic behaviour of a system with many particles ( $\sim 10^{23}$ ) e.g.  $P, T, V, S$

## Microcanonical ensemble

- Consider an isolated  $N$ -particle system ( $N$  large) with fixed energy  $E$ .
  - $\hookrightarrow$  instantaneously obeys  $H|\psi\rangle = E|\psi\rangle$ , where  $|\psi\rangle$  is the **microstate**, describing every particle's behaviour.
  - $\hookrightarrow$  a macro system can be made of many microstates with the same energy.

Fundamental assumption: in equilibrium, all accessible microstates are equally likely

- $\hookrightarrow$  equilibrium  $\rightarrow$  steady state with constant macro quantities
- $\hookrightarrow$  accessible  $\rightarrow$  can be reached by small perturb. (at fixed  $E$ )
- $\Omega(E)$  counts the number of states with energy  $E$
- Entropy:  $S(E) = k_B \ln \Omega(E)$ 
  - $\hookrightarrow$  if we combine systems with  $E_1, E_2$ ,  $\Omega(E_1, E_2) = \Omega(E_1)\Omega(E_2)$ 
    - $\Rightarrow$  entropy is additive:  $S(E_1, E_2) = S(E_1) + S(E_2)$
  - $\hookrightarrow S \propto N$  so it is an **extensive** quantity rule of thumb: imagine combining 2 identical systems

## 2<sup>nd</sup> law of thermodynamics

- Consider two isolated systems with  $E_1, E_2 \rightarrow$  bring together and allow them to exchange energy.  $E_{tot} = E_1 + E_2$  is fixed.
- Total num states is  $\Omega_1(E_1)\Omega_2(E_2)$  summed across every possible value of  $E_1 \in \{E_i\}$

$$\begin{aligned} \hookrightarrow \Omega(E_{tot}) &= \sum_{\{E_i\}} \Omega_1(E_i)\Omega_2(E_{tot}-E_i) \\ &= \sum_{\{E_i\}} \exp\left(\frac{S_1(E_i)}{k_B} + \frac{S_2(E_{tot}-E_i)}{k_B}\right) \end{aligned}$$

- $\hookrightarrow$  the sum will be dominated by the  $E_i = E_*$  that maximises the exponent.  $\frac{\partial S_1}{\partial E} \Big|_{E=E_*} - \frac{\partial S_2}{\partial E} \Big|_{E=E_{tot}-E_*} = 0$

$$\begin{aligned} \hookrightarrow S(E_{tot}) &= k_B \ln \Omega(E_{tot}) \approx S_1(E_*) + S_2(E_{tot}-E_*), \text{ but} \\ S_1(E_*) + S_2(E_{tot}-E_*) &\geq S_1(E_1) + S_2(E_2) \text{ by def. of } E_* \\ \Rightarrow S(E_{tot}) &\geq S_1(E_1) + S_2(E_2) \leftarrow \text{2<sup>nd</sup> law} \end{aligned}$$

## Temperature

- Define as  $\frac{1}{T} \equiv \frac{\partial S}{\partial E}$ . This satisfies 0<sup>th</sup> law (no energy transfer between equal temps):
  - $\hookrightarrow T_1 = T_2 \Rightarrow \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \rightarrow$  this is the condition for max entropy
  - $\hookrightarrow$  entropy already maximised  $\Rightarrow$  no energy transfer.
- If  $T_1 \neq T_2$ , there will be an energy transfer
  - $\hookrightarrow \delta S = \frac{\partial S_1}{\partial E} \Big|_{E=E_1} \delta E_1 + \frac{\partial S_2}{\partial E} \Big|_{E=E_2} \delta E_2$ 

$$= \delta E_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0$$
  - $\hookrightarrow$  so if  $T_1 > T_2$ ,  $\delta E_1 < 0$  (hot  $\rightarrow$  cold)

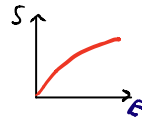
- $T$  can be negative if  $S \downarrow$  as  $E \uparrow$ , e.g. spin systems
  - ↳ in practice, these systems are coupled with surroundings with  $T > 0$
  - ↳ negative  $T$  'hotter' than infinite  $T$

• The heat capacity (at constant volume) is  $C_v = \frac{\partial E}{\partial T}$

↳ allows us to relate  $S$  to measurable quantities

$$\frac{\partial S}{\partial T} = \frac{\partial S}{\partial E} \frac{\partial E}{\partial T} = \frac{C_v}{T} \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_v(T)}{T} dT$$

↳  $\frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2 C_v}$ , so if  $C_v > 0$ ,  $S(E)$  is concave-down

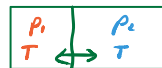


- General procedure for analysing a system:
  1. Count  $\Omega(E)$  using combinatorics ↳ which combinations of  $N_1, N_2, \dots$  have energy  $E$
  2. Find  $S(E)$  using the Boltzmann entropy
  3. Approximate factorials with Stirling's formula:  $\ln N! \approx N \ln N - N$
  4. Replace  $N_1, N_2, \dots$  with  $N_{total}$  and  $E$
  5. Find temp. with  $\frac{1}{T} = \frac{\partial S}{\partial E}$ , and invert to get  $E(T)$ .

### 1st Law of Thermodynamics

- Num. states depends on the volume  $V$ .
  - ↳  $S(E, V) = k_B \ln \Omega(E, V)$
  - ↳ as before  $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$
  - ↳ we define pressure to be  $T \left(\frac{\partial S}{\partial V}\right)_E$

• Consider bringing together systems with  $P_1, P_2$  (same  $T$ ) with a movable partition (but  $V_{tot} = const$ )



- ↳ maximizing entropy:  $\left(\frac{\partial S_1}{\partial V}\right)_{V_1} = \left(\frac{\partial S_2}{\partial V}\right)_{V_2} \Rightarrow P_1 = P_2$
- ↳ agrees with physical intuition.

• Use definitions of  $T, P$  to derive the 1st law:

$$S = S(E, V) \Rightarrow dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

$$\Rightarrow dE = T dS - p dV$$

heat transferred to system  $\leftarrow$  work done on system  $\leftarrow$   
at fixed temperature

microcanonical had fixed energy

### Canonical Ensemble

- Consider an ensemble in thermal eq. with large reservoir  $R$  with temp.  $T$ 
  - ↳ sys has negligible energy compared to  $R$
  - ↳ energy of system is no longer fixed



- Let  $|n\rangle$  be a state of sys with energy  $E_n$ . The num. of microstates in  $sys+R$  can be found by summing over states ↳ not energies like before
  - ↳  $\Omega(E_{tot}) = \sum_n \Omega_R(E_{tot} - E_n)$  ↳ can have duplicate  $E_n$
  - $= \sum_n \exp\left[\frac{1}{k_B} S_R(E_{tot} - E_n)\right]$

↳ but  $E_{tot} \gg E_n$  so we can Taylor expand  $S_R(E_{tot} - E_n)$

$$\Rightarrow \Omega(E_{tot}) = \sum_n \exp\left[\frac{1}{k_B} \left(S_R(E_{tot}) - \frac{\partial S}{\partial E} \Big|_{E=E_{tot}} E_n\right)\right]$$

$$= \exp\left[\frac{S_R(E_{tot})}{k_B}\right] \sum_n \exp\left(-\frac{E_n}{k_B T}\right)$$

• The probability that sys is in state  $|n\rangle$  is:

$$P(n) = \frac{\text{num states with } E_n}{\text{total num states}} \Rightarrow P(n) = \frac{e^{-E_n/k_B T}}{\sum_m e^{-E_m/k_B T}} \equiv \frac{1}{Z(\beta)} e^{-\beta E_n}$$



↳ this is the Boltzmann distribution.

↳  $\beta \equiv \frac{1}{k_B T}$  and  $Z(\beta) = \sum_m e^{-\beta E_m}$  is the partition function

↳ if  $\beta E_n \gg 1$ ,  $P(n)$  is small.

↳ if  $\beta E_n \ll 1$ ,  $P(n)$  is closer to 1.

VERY USEFUL.

• The partition function of a combined system is the product of the subsystems:  $Z = \sum_{n_1, m} \exp(-\beta E_{n_1}^{(1)} - \beta E_m^{(2)}) = \sum_{n_1} e^{-\beta E_{n_1}^{(1)}} \sum_m e^{-\beta E_m^{(2)}} = Z_1 Z_2$

• Energy in the canonical ensemble:

$$\hookrightarrow \langle E \rangle = \sum_n p(n) E_n = \frac{1}{Z} \sum_n E_n e^{-\beta E_n} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \Rightarrow \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$\hookrightarrow \text{similarly, } (\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\hookrightarrow \text{the heat capacity is } C_V = \frac{\partial \langle E \rangle}{\partial T} = (\Delta E)^2 / k_B T^2$$

•  $C_V \propto (\Delta E)^2$  is extensive  $\Rightarrow \Delta E \propto \sqrt{N}$ .

↳ energy is extensive:  $\Rightarrow \frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}}$

↳ in the thermodynamic limit ( $N \rightarrow \infty$ ),  $\frac{\Delta E}{E} \rightarrow 0$ , i.e. the

fluctuations around the avg are small

↳ we thus write  $\langle E \rangle = E$

↳ in this limit, canonical  $\leftrightarrow$  microcanonical ensembles are equivalent.

### Gibbs Entropy

•  $S = k_B \ln \Omega$  is only true in the microcanonical ensemble.

• Trick to derive  $S$  for a general system: consider a micro. ensemble consisting of  $W$  copies of the system ( $W \gg 1$ )

↳  $p(n)W$  systems have state  $|n\rangle$

↳ no. of arrangements of states among copies:  $\Omega = \frac{W!}{\prod_n (p(n)W)!}$

$$\hookrightarrow S_W = k_B \ln \Omega = -k_B W \sum_n p(n) \ln p(n) \quad (\text{Stirling})$$

↳ entropy is additive  $\therefore$  for one system,  $S = \frac{S_W}{W}$

↳ gives  $S = -k_B \sum_n p(n) \ln p(n)$  ← Gibbs entropy (aka Shannon, von Neumann)

### Free energy

• When  $T=0$ , the ground state minimises energy.

• Generally, the most likely state minimises the Helmholtz Free energy

$$\hookrightarrow F = E - TS$$

↳  $F$  is the capacity to do work (at fixed temperature).

• Proof:

$$\hookrightarrow \text{prob. that system has energy } E \text{ is } P(E) = \frac{\text{num of states with energy } E}{Z} e^{-E/k_B T} = \frac{\Omega(E)}{Z} e^{-E/k_B T}$$

$$\hookrightarrow P(E) = \frac{1}{Z} e^{S/k_B} e^{-E/k_B T} = \frac{1}{Z} e^{-\beta F}$$

↳ so to maximise  $p(E)$ , minimise  $F$ .

•  $F$  is a Legendre transformation of  $S(E, V)$ :

$$\hookrightarrow F = E - TS \Rightarrow dF = dE - TdS = -SdT - pdV$$

$$\hookrightarrow \text{most natural to consider } F = F(T, V) \Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V, P = -\left(\frac{\partial F}{\partial V}\right)_T$$

• Can show that  $F = -k_B T \ln Z \Rightarrow Z = e^{-\beta F}$

## Chemical Potential

- In some systems, num particles  $N$  may change (e.g permeable membrane)
  - $\hookrightarrow S(E, V, N) = k_B \ln \Omega(E, V, N)$
  - $\hookrightarrow$  define the **chemical potential** to be  $\mu \equiv -T \frac{\partial S}{\partial N}$
  - $\hookrightarrow \mu_1 = \mu_2$  in equilibrium
- The 1<sup>st</sup> law becomes  $dE = TdS - pdV + \mu dN$ 
  - $\hookrightarrow$  i.e  $\mu$  is the energy cost of adding a particle at fixed  $S, V$ 
    - $\Rightarrow \mu = \left( \frac{\partial E}{\partial N} \right)_{S, V}$
  - $\hookrightarrow$  Helmholtz free energy:  $dF = -SdT - pdV + \mu dN$

## Grand Canonical Ensemble

- The **Grand Canonical Ensemble** is in thermodynamic eq with a large reservoir of fixed  $\mu$  and  $T$ 
  - $\hookrightarrow$  particle num. can now fluctuate in addition to energy.
  - $\hookrightarrow$  reservoir much larger than system
- Prob. that system is in microstate  $|n\rangle$  with  $E_n, N_n$  is:
 

$$p(n) = \frac{1}{Z(T, \mu, V)} e^{-\beta(E_n - \mu N_n)}, \quad Z = \sum_n e^{-\beta(E_n - \mu N_n)}$$

  - $\hookrightarrow Z$  is the **grand partition function**, from which other quantities can be derived
    - $\hookrightarrow \langle E \rangle - \mu \langle N \rangle = -\frac{\partial}{\partial \beta} \ln Z, \quad \langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z$
- All three canonical ensembles coincide in the thermodynamic limit.
- The **grand canonical potential** is  $\Phi \equiv F - \mu N \Rightarrow d\Phi = -SdT - pdV - Nd\mu$ 
  - $\hookrightarrow \Phi = -k_B T \ln Z \Rightarrow Z = e^{-\beta \Phi}$  ← same form as canonical with  $F$ .

## Extensive vs Intensive quantities

- Extensive quantities scale with the size of the system
  - $\hookrightarrow$  e.g  $N, V, E, S$
  - $\hookrightarrow$  for each of these, can write  $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N), \lambda \in \mathbb{R}$
- Intensive quantities are independent of size, e.g  $\frac{1}{T} = \frac{\partial S}{\partial E}, p = T \frac{\partial S}{\partial V}, \mu = -T \frac{\partial S}{\partial N}$
- Extensive  $\times$  intensive = extensive
  - $\hookrightarrow$  e.g  $F = E - TS$  is extensive  $\Rightarrow F(T, \lambda V, \lambda N) = \lambda F(T, V, N)$
  - $\hookrightarrow$  many functional forms satisfy this, e.g  $F \sim V^{n+1}/N^n$
- $\Phi = F - \mu N$  is extensive  $\Rightarrow \Phi(T, \lambda V, \mu) = \lambda \Phi(T, V, \mu)$ 
  - $\hookrightarrow$  unlike for  $F$ , this is only true if  $\Phi \propto V$
  - $\hookrightarrow$  but  $\left( \frac{\partial \Phi}{\partial V} \right)_{T, \mu} = -p \Rightarrow \Phi = -p(T, \mu) V$

# Classical Gases

- The quantum partition func is  $Z = \sum_{\text{states}} e^{-\beta E_n}$
- Classically, specify state with phase space coordinates of every particle
  - ↳ for a single particle  $H = \frac{1}{2m} |p|^2 + V(q)$
  - ↳ this gives  $Z_1 = \frac{1}{(2\pi\hbar)^3} \int d^3p d^3q e^{-\beta H} \leftarrow \text{derive from QM}$
- An ideal gas is  $N$  non-interacting particles in a box
  - ↳  $H = |p|^2/2m \Rightarrow Z_1(V, T) = \frac{1}{(2\pi\hbar)^3} \int d^3q d^3p \exp\left[-\frac{\beta |p|^2}{2m}\right]$
  - $= V \left(\frac{k_B T m}{2\pi\hbar^2}\right)^{3/2} \equiv \frac{V}{\lambda^3}$
  - ↳  $\lambda$  is the thermal de Broglie wavelength.
  - ↳ the partition function is then  $Z(N, V, T) = \frac{V^N}{\lambda^{3N}}$
- Pressure:  $p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\partial}{\partial V} k_B T \ln Z = \frac{N k_B T}{V} \leftarrow \text{ideal gas law}$
- Energy:  $\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} N k_B T$ 
  - ↳ equipartition theorem: classical systems have  $\frac{1}{2} k_B T$  avg energy per degree of freedom.
- Heat capacity:  $C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2} N k_B$
- We assumed  $Z = Z_1^N$ . This overcounts, because quantum particles are indistinguishable.  $Z_{\text{ideal}}(N, V, T) = \frac{Z_1^N}{N!} = \frac{V^N}{N! \lambda^{3N}}$
- ↳ doesn't change  $P$  or  $E$ , but affects entropy:
  - $S = \frac{\partial}{\partial T} (k_B T \ln Z) = N k_B \left[ \frac{5}{2} + \ln\left(\frac{V}{N \lambda^3}\right) \right] \leftarrow \text{Sackur-Tetrode equation}$
  - ↳ without the  $N!$ , entropy is not extensive  $\rightarrow$  the Gibbs paradox

- The partition function can be thought of as  $\sum_{\text{speeds}} \text{prob}(\text{speed})$
- for a single particle:  $Z_1 = \frac{1}{(2\pi\hbar)^3} \int d^3q d^3p e^{-\beta p^2/2m}$   
 $= \frac{m^3 V}{(2\pi\hbar)^3} \int dv \underbrace{v^2 e^{-\beta m v^2/2}}_{\text{prob. dist}}$

- Maxwell distr.:  $f(v)dv \propto v^2 e^{-m v^2/2k_B T}$

## Ideal gas in the Grand canonical ensemble

- $Z_{\text{ideal}}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_{\text{ideal}}(N, V, T) = \exp\left(\frac{e^{\beta \mu} V}{\lambda^3}\right)$
- Avg num particles:  $N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z = e^{\beta \mu} V / \lambda^3$ 
  - ↳  $\mu = k_B T \ln\left(\frac{\lambda^3 N}{V}\right)$  → not too close
  - ↳ for the gas to be classical, need  $\lambda \ll \left(\frac{V}{N}\right)^{1/3} \Rightarrow \mu < 0$
  - ↳ to keep  $S$  fixed when we add a particle,  $E$  must decrease
  - $\therefore \mu = \left(\frac{\partial E}{\partial N}\right)_{S, V} < 0$
- Equation of state:
  - ↳ grand potential  $\Phi = -k_B T \ln Z = -pV$
  - ↳  $pV = k_B T \frac{e^{\beta \mu} V}{\lambda^3} = N k_B T \rightarrow \text{recovers ideal gas law}$

## Diatomic gas

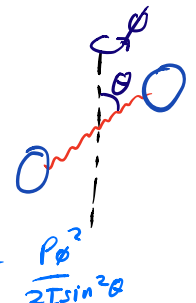
- Diatomic molecules have additional degrees of freedom

- Rotations:  $\mathcal{L}_{\text{rot}} = \frac{1}{2} I (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2)$

↳ canonical momenta:  $p_{\theta} = \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = I \dot{\theta}$

$p_{\phi} = \frac{\partial \mathcal{L}}{\partial \dot{\phi}} = I \sin^2 \theta \dot{\phi}$

↳ Hamiltonian:  $H_{\text{rot}} = \dot{\theta} p_{\theta} + \dot{\phi} p_{\phi} - \mathcal{L} = \frac{p_{\theta}^2}{2I} + \frac{p_{\phi}^2}{2I \sin^2 \theta}$



$$\begin{aligned} \hookrightarrow Z_{rot} &= \frac{1}{(2\pi\hbar)^2} \int d\theta d\phi d p_\theta d p_\phi e^{-\beta H_{rot}} \\ &= 2I k_B T / \hbar^2 \end{aligned}$$

$\hookrightarrow \langle E_{rot} \rangle = -\frac{\partial}{\partial \beta} \ln Z_{rot} = k_B T$ , i.e. rotation provides an additional 2 d.o.f  $\leftarrow$  assume  $I_z = 0$  along symmetry axis

• Vibrations: model as harmonic oscillator 

$$\hookrightarrow H_{vib} = \frac{p_x^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$\hookrightarrow Z_{vib} = \frac{1}{2\pi\hbar} \int dx dp_x e^{-\beta H_{vib}} = \frac{k_B T}{\hbar \omega}$$

$\hookrightarrow \langle E_{vib} \rangle = k_B T \Rightarrow$  vibration provides 2 d.o.f

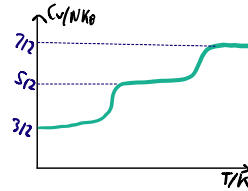
• The overall partition function is  $Z_1 = Z_{trans} Z_{rot} Z_{vib}$

$\hookrightarrow$  expect the heat capacity to be  $C_V = \frac{7}{2} N k_B$

$\hookrightarrow$  but experimentally we observe a changing value

$\hookrightarrow$  at lower temps, some modes 'freeze'

$\hookrightarrow$  this is a QM effect.



### Interacting gas

• Ideal gas law is appropriate for small number densities.

• General eq. of state from the virial expansion:

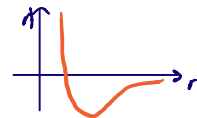
$$\frac{p}{k_B T} = \frac{N}{V} + \beta_2(T) \left(\frac{N}{V}\right)^2 + \beta_3(T) \left(\frac{N}{V}\right)^3 + \dots$$

• Objective is to compute the virial coefficients  $\beta_i(T)$

• Model the interaction between neutral atoms with the Lennard-Jones potential

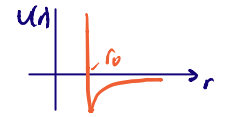
$$U(r) = \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6$$

$\uparrow$  Pauli repulsion
 $\uparrow$  Van der Waals



$\hookrightarrow$  alternatively, can use hard core repulsion

$$U(r) = \begin{cases} \infty & r < r_0 \\ -U_0 \left(\frac{r_0}{r}\right)^6 & r > r_0 \end{cases}$$



• The Hamiltonian is  $H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i;j} U_{ij} \leftarrow U_{ij} \equiv U(|r_i - r_j|)$

$\hookrightarrow$  because of the interactions,  $Z$  can't be factorised into individual particle partition fns

$$\begin{aligned} Z(N, V, T) &= \frac{1}{N!} \left(\frac{1}{2\pi\hbar}\right)^{3N} \int \prod_{i=1}^N d^3 p_i d^3 r_i e^{-\beta H} \\ &= \frac{1}{N!} \left(\frac{1}{2\pi\hbar}\right)^{3N} \left[ \prod_i d^3 p_i e^{-\beta p_i^2 / 2m} \right] \left[ \int \prod_i d^3 r_i \exp\left(-\beta \sum_{j>k} U_{jk}\right) \right] \end{aligned}$$

$$Z(N, V, T) = \frac{1}{N!} \frac{1}{\lambda^{3N}} \int \prod_i d^3 r_i \exp\left(-\beta \sum_{j>k} U_{jk}\right)$$

• To proceed, define the Mayer F function:  $f(r) = e^{-\beta U(r)} - 1$

$\hookrightarrow f(r) \rightarrow 0$  as  $r \rightarrow \infty$

$\hookrightarrow f(r) \rightarrow -1$  as  $r \rightarrow 0$  (avoids singularity)

$$\begin{aligned} \Rightarrow Z(N, V, T) &= \frac{1}{N!} \frac{1}{\lambda^{3N}} \int \prod_i d^3 r_i \prod_{j>k} (1 + f_{jk}) \\ &= \frac{1}{N!} \frac{1}{\lambda^{3N}} \left( 1 + \sum_{j>k} f_{jk} + \sum_{j>k, l>m} f_{jk} f_{lm} + \dots \right) \end{aligned}$$

$$\hookrightarrow \int \prod_i d^3 r_i 1 = V^N$$

$$\hookrightarrow \int \prod_i d^3 r_i f_{jk} = V^{N-1} \int d^3 r f(r), \text{ after changing to relative coordinates with } r = r_j - r_k$$

$\hookrightarrow$  independent of  $j, k$  and there are  $\frac{1}{2} N^2$  pairs

$$\Rightarrow Z(N, V, T) = \frac{V^N}{N! \lambda^{3N}} \left( 1 + \frac{1}{2} \frac{N^2}{V^2} \int d^3 r f(r) + \dots \right)$$

## Quantum Gases

- Can thus write the 2<sup>nd</sup> order partition func as:

$$Z(N, V, T) = Z_{\text{ideal}} \left( 1 + \frac{N}{2V} \int d^3r f(r) \right)^N$$

↳ free energy  $\rightarrow F = -k_B T \ln Z = F_{\text{ideal}} - N k_B T \ln \left( 1 + \frac{N}{2V} \int d^3r f(r) \right)$

↳ can find other quantities using  $\ln(1+x) \approx x$

↳  $p = -\frac{\partial F}{\partial V} \Rightarrow \frac{pV}{N k_B T} = 1 - \frac{N}{2V} \int d^3r f(r) + \dots$   
 $\frac{N}{2} \times$  virial coefficient  $b_2(T)$

- For a repulsive force,  $U(r) > 0 \Rightarrow f(r) < 0$ , so pressure increases.

- Using the hard-core repulsion model at high temperatures, we get

the van der Waals equation of state  $k_B T = \left( p + \frac{N^2 a}{V^2} \right) \left( \frac{V}{N} - b \right)$

↳ can rewrite as  $p = \frac{N k_B T}{V - bN} - a \frac{N^2}{V^2}$   
reduced vol. due to repulsion  $\rightarrow$   $\rightarrow$  reduced  $p$  due to attraction

↳  $b = 2\pi r_0^3/3 \approx$  excluded volume. The extra factor

of  $1/2$  comes from considering cfg space

↳ add atoms one at a time:  $\frac{1}{N!} V(V - V_{\text{exc}})(V - 2V_{\text{exc}}) \dots (V - (N-1)V_{\text{exc}})$



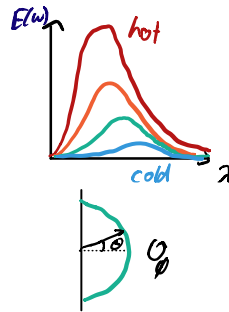
- Consider gas in a cubic box ( $V=L^3$ ) with periodic B.C.s
- For non-interacting particles,  $\Psi = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$  with  $k_i = \frac{2\pi n_i}{L}$ ,  $n_i \in \mathbb{Z}$ 
  - ↳ non-relativistic particles:  $E_n = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$
  - ↳  $\beta E_n = \frac{\pi^2 \lambda^2 n^2}{L^2} \rightarrow L \gg \lambda$  so energy levels are finely spaced.
  - ↳ approximate sums as integrals:  $\sum_n \approx \int dn = \left(\frac{V}{2\pi}\right)^3 \int d^3k$
  - ↳ in spherical coordinates in  $k$ -space,  $\int d^3k = 4\pi \int_0^\infty dk k^2$
  - ↳ the state density  $g(E)$  is such that  $g(E)dE$  is the num. of states with energy  $E \rightarrow E+dE$ .
  - ↳  $\int d^3n = \int_0^\infty g(E)dE \Rightarrow g(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$
- For relativistic systems,  $E = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4} \Rightarrow g(E) = \frac{VE}{2\pi^2 \hbar^3 c^3} \sqrt{E^2 - m^2 c^4}$ 
  - ↳ for massless particles,  $g(E) = \frac{V}{2\pi^2 \hbar^3 c^3} E^2$

### Photon gas

- A gas of photons at fixed  $T$  is called black-body radiation
- $E = \hbar\omega$ , with  $\lambda = \frac{2\pi c}{\omega} \Rightarrow g(E)dE = 2 \cdot \frac{VE^2}{2\pi^2 \hbar^3 c^3}$  polarisations
  - ↳  $g(\omega)d\omega = \frac{V\omega^2}{\pi^2 c^3} d\omega$
  - ↳ photons are not conserved  $\Rightarrow$  photon num not fixed. ← must sum over  $N$  in partition func.
- For fixed  $\omega$ ,  $Z_\omega = \sum_{N=0}^{\infty} e^{-N\beta\hbar\omega} = (1 - e^{-\beta\hbar\omega})^{-1}$ 
  - ↳ overall partition func:  $Z = z_1 z_2 \dots z_n \Rightarrow \ln Z = \sum \ln z_i = \int \ln z_i$
  - $\ln Z = \int_0^\infty d\omega g(\omega) \ln Z_\omega = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \omega^2 \ln(1 - e^{-\beta\hbar\omega})$
  - ↳ energy:  $E = -\frac{\partial}{\partial \beta} \ln Z = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$

- Planck distribution:  $E(\omega)d\omega = \frac{V\hbar}{\pi^2c^3} \frac{\omega^3}{e^{\beta\hbar\omega}-1} d\omega$ 
  - ↳ max when  $\frac{dE}{d\omega} = 0 \Rightarrow \lambda_{\max} = \frac{b}{T} \leftarrow$  Wien's law
  - ↳ total energy density:  $E = \frac{E}{V} = \frac{\pi^2 k_B^4}{15\hbar^3c^3} T^4$
- Energy flux from a point on the surface:
  - ↳  $E \cdot \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} (c \cos\theta) \sin\theta d\theta = \frac{Ec}{4}$ 

normal component.
  - ↳ gives the Stefan-Boltzmann law:  $\text{flux} = \frac{Ec}{4} = \sigma T^4$
- Classically, the world is continuous  $\Rightarrow \hbar\omega \ll k_B T$ 
  - ↳  $\frac{1}{e^{\beta\hbar\omega}-1} \approx \frac{1}{\beta\hbar\omega} \Rightarrow E(\omega) \approx \frac{V\omega^2 k_B T}{\pi^2 c^3}$
  - ↳ this is the Rayleigh-Jeans law (classical)
  - ↳ leads to the ultraviolet catastrophe because it diverges at small  $\lambda$



- The Debye temperature is  $k_B T_D = \hbar\omega_D$ 
  - ↳ temp. at which the highest freq phonon becomes excited
  - ↳  $T_D \sim$  hundreds of kelvin (higher for harder materials).
- Phonons are not conserved  $\Rightarrow$  similar partition func to photons
  - ↳  $Z_\omega = (1 - e^{-\beta\hbar\omega})^{-1}$  (same as photon)
  - ↳  $\ln Z_{\text{phon}} = \int_0^{\omega_D} d\omega g(\omega) \ln Z_\omega$  (integrate up to  $\omega_D$ , not  $\infty$ )
  - ↳  $\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$ 

$$= \frac{3V\hbar}{2\pi^2c^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta\hbar\omega}-1} d\omega = \frac{3V}{2\pi^2(\hbar c)^3} (k_B T)^4 \int_0^{T_D/T} \frac{x^3}{e^x-1} dx$$

- For low temp ( $T \ll T_D$ ),  $C_V \propto T^3$ . This explains the *Dulong-petit* law, which previous models failed to predict.
- For high temp  $C_V \rightarrow 3Nk_B$  as required.
- In most materials the heat capacity is dominated by phonon modes.

## Debye Model of Phonons

- Vibrations in a solid come in discrete packets of energy - **phonons**
  - ↳  $E = \hbar\omega \approx \hbar|k|c_s \leftarrow$  valid for small  $|k| \leftarrow$  linear approx to dispersion relation
  - ↳ phonons have 3 polarisations: 2 transverse + 1 longitudinal
  - ↳ density of states  $g(\omega) = 3 \cdot \frac{V\omega^2}{2\pi^2c_s^3}$
  - ↳ minimum wavelength is lattice spacing  $\rightarrow$  max freq  $\omega_D$  Debye freq.
- The Debye model determines  $\omega_D$ :
  - ↳ equate the num. of single phonon states with the d.o.f (both count the num. of possible excitations)
  - ↳  $3N = \int_0^{\omega_D} g(\omega)d\omega = \frac{3V\omega_D^3}{2\pi^2c_s^3} \Rightarrow \omega_D = c_s (6\pi^2)^{1/3} \left(\frac{N}{V}\right)^{1/3}$
  - ↳ can associate a characteristic energy/temp with  $\omega_D$

## Diatomic gas (QM correction)

- The classical  $C_V = \frac{5}{2}Nk_B$  only agrees with experiment for high  $T$  because d.o.f 'freeze out' at lower temp.
- e.g for rotation,  $E = \frac{\hbar^2}{2I} j(j+1)$ ,  $j = 0, 1, 2, \dots$  with degen  $2j+1$ 
  - ↳  $Z_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) \exp(-\beta\hbar^2 j(j+1)/2I)$
  - ↳ when  $T \gg \hbar^2/2Ik_B$ , sum  $\rightarrow$  integral  $\therefore Z_{\text{rot}} \approx \frac{2I}{\beta\hbar^2}$  same as classical
  - ↳ but for  $T \ll \hbar^2/2Ik_B$ ,  $Z_{\text{rot}} \approx 1$  so rotational modes are 'frozen'.
- Similar analysis for vibrational modes with  $E = \hbar\omega(n + \frac{1}{2})$ .

# Bose-Einstein Distribution

- Bosons have exchange-symmetric wavefunctions:  $\Psi(r_1, r_2) = \Psi(r_2, r_1)$
  - Label single-particle states such that  $H|r\rangle = E_r|r\rangle$ , with  $n_r$  particles in each  $|r\rangle$
  - Canonical ensemble: sum over sets  $\{n_r\}$  s.t.  $\sum_r n_r = N$   
 $Z = \sum_{\{n_r\}} e^{-\beta \sum_r n_r E_r}$  ← difficult because of  $\{n_r\}$
  - Easier to work in grand canonical. For a given state  $|r\rangle$ :  
 $Z_r = \sum_{n_r} e^{-\beta n_r (E_r - \mu)} = (1 - e^{-\beta(E_r - \mu)})^{-1}$
- ↳ converges for  $E_r - \mu > 0$  for all states.  $E_0 = 0 \Rightarrow \mu < 0$
- ↳ state occupations are independent of each other:

$$Z_{\text{grand}} = \prod_r \frac{1}{1 - e^{-\beta(E_r - \mu)}}$$

- ↳  $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{\text{grand}} = \sum_r \frac{1}{e^{\beta(E_r - \mu)} - 1} \equiv \sum_r \langle n_r \rangle$
- ↳ so the avg num of particles in  $|r\rangle$  is:  $n_r = \frac{1}{e^{\beta(E_r - \mu)} - 1}$  → Bose-Einstein Distr.
- ↳ fugacity:  $z \equiv e^{\beta \mu}$ . For boson gas,  $0 < z < 1$
- Total num. of particles:  $N(\mu, T, V) = \int dE n g(E) = \int dE \frac{g(E)}{z^{-1} e^{\beta E} - 1}$
  - Pressure:  $pV = \frac{1}{\beta} \ln Z_r = -\frac{1}{\beta} \int dE g(E) \ln(1 - z e^{-\beta E})$   
 ↳  $g(E) \propto E^{1/2}$  so integrate by parts  $pV = \frac{2}{3} \int dE \frac{E g(E)}{z^{-1} e^{\beta E} - 1}$   
 $\Rightarrow pV = \frac{2}{3} E$

## High-temperature boson gas

- Consider the  $z = e^{\beta \mu} \ll 1$  limit:

$$\frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty dE \frac{E^{1/2}}{z^{-1} e^{\beta E} - 1} = [\dots] \int_0^\infty dE \frac{z e^{-\beta E} E^{1/2}}{1 - z e^{-\beta E}}$$

- ↳ let  $x = \beta E = u^2$  and expand ← Gaussian integrals  
 $\Rightarrow \frac{N}{V} = \frac{2}{\lambda^3} (1 + z \cdot \frac{1}{2\sqrt{2}} + \dots)$  (\*) ← c.f. need  $z$  large
- ↳ expansion only consistent if  $\lambda^3 N \ll 1 \Rightarrow \lambda^3 \ll \frac{V}{N}$
- ↳ this is thus the high temp. expansion
- ↳ i.e. at constant  $N$ ,  $\mu$  must change:  $\frac{N}{V} = \text{const} \Rightarrow \frac{z}{\lambda^3} = \text{const}$   
 $\Rightarrow z \propto T^{-3/2}$

- To get the EOS, we need another expression for  $E$ :

$$\frac{E}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty dE \frac{E^{3/2}}{z^{-1} e^{\beta E} - 1} \stackrel{\text{sub } x = \beta E = u^2}{=} \dots = \frac{3z}{2\lambda^3 \beta} \left(1 + \frac{z}{4\sqrt{2}} + \dots\right)$$

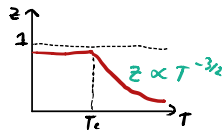
- ↳ eliminate small  $z$  using inverted (\*)  
 $\Rightarrow E = \frac{3}{2} \frac{N}{\beta} \left(1 - \frac{1}{2\sqrt{2}} \frac{\lambda^3 N}{V} + \dots\right) \left(1 + \frac{1}{4\sqrt{2}} \frac{\lambda^3 N}{V} + \dots\right)$
- ↳ sub  $pV = \frac{2}{3} E \Rightarrow pV = Nk_B T \left(1 - \frac{\lambda^3 N}{4\sqrt{2}V} + \dots\right)$

- ↳ at high temp, classical ideal gas is recovered



## Low-temperature limit (Bose-Einstein Condensation)

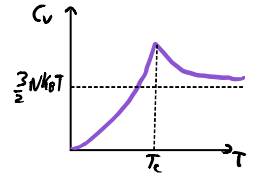
- For low temp,  $z \rightarrow 1$ .
- $\frac{N}{V} = \frac{1}{4\pi^2} \left( \frac{2mk_B T}{\hbar^2} \right)^{3/2} \int_0^\infty dx \frac{x^{1/2}}{z^{-1}e^x - 1} \equiv \frac{1}{\lambda^3} g_{3/2}(z)$
- $g_n(z)$  is a polylogarithm:  $g_n(z) \equiv \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{z^{-1}e^x - 1}$ 
  - ↳ as  $z \rightarrow 0$ ,  $g_{3/2}(z) \rightarrow 0$
  - ↳  $g_n(z)$  is a monotonically increasing function of  $z$  ← convert integral to sum
  - ↳  $g_n(1) = \zeta(n)$  (Riemann zeta function)
- As  $T \downarrow$  there will be some  $T=T_c$  for which  $z=1$ :
  - ↳ sub  $z=1$ :  $\frac{N}{V} = \left( \frac{mk_B T_c}{2\pi\hbar^2} \right)^{3/2} \zeta\left(\frac{3}{2}\right)$
  - ↳ for  $T < T_c$ , it seems that  $\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z)$  should decrease since  $\lambda \uparrow$ , i.e. particles disappear.
- The mistake was approximating the sum over states as an integral
  - ↳  $\sum_n \propto \int dE E^{1/2}$  gives zero weight to the ground state
  - ↳ as  $T \downarrow$ , the particles are condensing into the ground state
  - ↳ B-E distr:  $n_0 = \frac{1}{z^{-1}-1}$ , so as  $z \rightarrow 1$ ,  $n_0$  gets large.
- Including the ground state  $\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z) + \frac{1}{z^{-1}-1}$ 
  - ↳  $N$  is fixed as  $T \rightarrow 0$
  - ↳ for finite  $N$ ,  $z \rightarrow 1 - \frac{1}{N}$  as  $T \rightarrow 0$
  - ↳ frac. of particles in the ground state is  $\frac{n_0}{N} \propto 1 - \frac{\sqrt{V}}{N\lambda^3} \zeta(3/2) = 1 - \left(\frac{T}{T_c}\right)^{3/2}$
  - ↳ at low  $T$ , a macroscopic num<sup>m</sup> of particles may be in the ground state
    - Bose-Einstein Condensate (BEC)
- EoS:  $P = \frac{2}{3} \frac{E}{V} = \frac{k_B T}{\lambda^3} g_{5/2}(z)$ 
  - ↳ for  $T < T_c$ ,  $z \approx 1 \Rightarrow P \approx \frac{k_B T}{\lambda^3} \zeta(5/2) \propto T^{5/2}$  (independent of  $\frac{N}{V}$ )



## Phase transitions

→ discontinuities in physical observables.

- BEC formation is a phase trans.
- For a boson gas,  $\frac{E}{V} = \frac{3}{2} \frac{k_B T}{\lambda^3} g_{5/2}(z)$ 
  - $\Rightarrow \frac{C_V}{V} = \frac{1}{V} \frac{dE}{dT} = \frac{15k_B}{4\lambda^3} g_{5/2}(z) + \frac{3}{2} \frac{k_B T}{\lambda^3} \frac{dg_{5/2}}{dz} \left( \frac{dz}{dT} \right) \rightarrow \approx 0$  for  $T < T_c$
  - ↳ for  $T < T_c$ ,  $\frac{C_V}{V} \sim T^{3/2}$
  - ↳  $C_V$  decreases for  $T > T_c \Rightarrow$  max at  $T = T_c$
  - ↳  $C_V = \frac{15\sqrt{V}k_B}{4\lambda^3} g_{5/2}(z) - b \left( \frac{T-T_c}{T_c} \right)$
- This discontinuity only exists in the  $N \rightarrow \infty$  limit.



# Fermi-Dirac Distribution

- Wavefunction is exchange antisymmetric:  $\Psi(\underline{r}_1, \underline{r}_2) = -\Psi(\underline{r}_2, \underline{r}_1)$
- Fermions obey Pauli exclusion  $\rightarrow$  any state occupied by 0 or 1 fermion
- A composite particle made of  $2N$  fermions acts as a boson
- Work in grand canonical:
  - $\hookrightarrow$  for a given state  $Z_r = \sum_{n=0,1} e^{-\beta n(E_r - \mu)} = 1 + e^{-\beta(E_r - \mu)}$
  - $\hookrightarrow Z = \prod_r Z_r \Rightarrow \langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z = \sum_r \frac{1}{e^{\beta(E_r - \mu)} + 1} \equiv \sum_r \langle n_r \rangle$
  - $\hookrightarrow$  this gives the Fermi-Dirac distr.:  $n_r = \frac{1}{e^{\beta(E_r - \mu)} + 1}$
  - $\hookrightarrow \mu$  can be either positive or negative.

## Ideal Fermi gas

- Non-interacting, non-relativistic:  $E = \frac{\hbar^2 k^2}{2m}$
- Fermions have degeneracy  $g_s = 2s + 1$  so the density of states is:
 

$$g(E) = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

  - $\hookrightarrow N = \int dE \frac{g(E)}{z^{-\beta E} + 1}$ ,  $E = \int dE \frac{E g(E)}{z^{-\beta E} + 1}$
  - $\hookrightarrow pV = k_B T \ln Z \Rightarrow pV = \frac{2}{3} E$  (same as bosons) ← increase in pressure
- High-temp expansion ( $z \ll 1$ ):  $pV = Nk_B T \left(1 + \frac{2^3 N}{4\sqrt{3} g_s V} + \dots\right)$

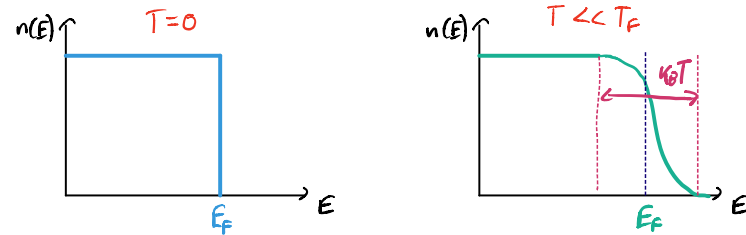
## Degenerate Fermi gas

- As  $T \rightarrow 0$ ,  $\frac{1}{e^{\beta(E-\mu)} + 1} \rightarrow \begin{cases} 1, & E < \mu \\ 0, & E > \mu \end{cases}$  } Degenerate Fermi gas
- $\hookrightarrow$  each fermion goes into the lowest-energy available state until all fermions have been used up
- $\hookrightarrow$  the Fermi energy  $E_F$  is the energy of the last filled state.
 

$E_F \equiv \mu(T=0)$

← at fixed  $N$
- $\hookrightarrow E_F$  in terms of  $N$ :  $N = \int_0^{E_F} dE g(E) = \frac{g_s V}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$   
 $\Rightarrow E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{g_s V}\right)^{2/3}$
- $E_F$  is the characteristic energy scale; there is an associated characteristic Fermi temperature  $T_F = E_F/k_B$  ←  $T < T_F$  is 'low' temp
- Fermi momentum  $k_F$ :  $E_F = \frac{\hbar^2 k_F^2}{2m}$ 
  - $\hookrightarrow$  states with  $|k| < k_F$  are filled  $\rightarrow$  Fermi sea
  - $\hookrightarrow$  states with  $|k| = k_F$  form the Fermi surface
- $T=0$   $E_0 S$ :  $pV = \frac{2}{3} E = \frac{2}{3} \int_0^{E_F} dE E g(E) = \frac{2}{3} N E_F$ 
  - $\hookrightarrow$  pressure nonzero even at  $T=0 \rightarrow$  degeneracy pressure

## Low temperature Fermi gas ( $T \ll T_F$ )



- We are interested in  $E(T)$ . We have  $\frac{E}{V} = \frac{g_V}{4\pi} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\infty} dE \frac{E^{3/2}}{e^{\beta(E-\mu)} + 1}$
- For  $N$  fixed, we must have  $\frac{d\mu}{dT}|_{T=0} = 0$ 
  - $\hookrightarrow \frac{dN}{dT} = \frac{d}{dT} \int_0^{\infty} dE \frac{g(E)}{e^{\beta(E-\mu)} + 1} = \int_0^{\infty} dE g(E) \frac{d}{dT} \left( \frac{1}{e^{\beta(E-\mu)} + 1} \right)$
  - $\hookrightarrow \frac{d}{dT} [\dots]$  only nonzero (approximately) near  $E_F$ , so  $g(E) \rightarrow g(E_F)$
  - $\hookrightarrow$  replace  $\mu$  by  $E_F$  since  $T$  small
  - $\therefore \frac{dN}{dT} \approx g(E_F) \int_0^{\infty} dE \underbrace{\left(\frac{E-E_F}{k_B T}\right)^2}_{\text{odd about } E_F} \frac{1}{\underbrace{\cosh^2(\beta(E-E_F)/2)}_{\text{Even about } E_F}} \approx 0$
- Heat capacity:  $C_V = \frac{\partial E}{\partial T} \Big|_{N,V} = \int_0^{\infty} dE E g(E) \frac{\partial}{\partial T} \frac{1}{e^{\beta(E-\mu)} + 1}$ 
  - $\hookrightarrow$  Taylor expand  $E g(E) = E_F g(E_F) + \frac{3}{2} g(E_F) (E-E_F)$
  - $\hookrightarrow C_V = \frac{3}{2} g(E_F) T \int_{-\infty}^{\infty} dx \frac{x^2}{4 \cosh^2(x/2)} \Rightarrow C_V \sim g(E_F) T \sim N k_B \frac{T}{T_F}$
  - $\hookrightarrow$  linear because only the fermions within  $k_B T$  of  $E_F$  participate; if each acquires energy  $k_B T$ ,  $E \sim g(E_F) k_B T \cdot k_B T \Rightarrow C_V \sim g(E_F) T$
- Electrons in metals can be modelled as free Fermi gas
  - $\hookrightarrow$  heat capacity for a metal:  $C_V = \gamma T + \alpha T^3$ 
    - $\uparrow$  electrons
    - $\uparrow$  phonons
  - $\hookrightarrow$  phonons dominate at high  $T$

## Pauli paramagnetism

- External magnetic fields cause electron spins to align:
  - $E_{\text{spin}} = \mu_B \underline{B} \cdot \underline{s}$ , where  $\mu_B \equiv \frac{e\hbar}{2mc}$  is the Bohr magneton and  $s = \pm 1$
  - $\uparrow$  and  $\downarrow$  now have different occupations:
    - $\frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\infty} dE \frac{1}{e^{\beta(E \pm \mu_B B - \mu)} - 1}$
- Magnetisation measures how energy changes with  $B$ :  $M = -\frac{\partial E}{\partial B}$ 
  - $\hookrightarrow E = E_0 + \mu_B B N_{\uparrow} - \mu_B B N_{\downarrow} \Rightarrow M = -\mu_B (N_{\uparrow} - N_{\downarrow})$
  - $\hookrightarrow$  Magnetic susceptibility:  $\chi \equiv \frac{\partial M}{\partial B}$   $\leftarrow$  how easy to magnetise
- At high temperatures,  $z \rightarrow 0 \Rightarrow \frac{N}{V} \rightarrow \frac{z}{\lambda^3} e^{\pm \beta \mu_B B}$ 
  - $\Rightarrow M \approx \frac{2\mu_B V z}{\lambda^3} \sinh(\beta \mu_B B)$
  - $\hookrightarrow N = N_{\uparrow} + N_{\downarrow} \approx \frac{2V z}{\lambda^3} \cosh(\beta \mu_B B)$  so we can eliminate  $z$ 
    - $\Rightarrow M \approx \mu_B N \tanh(\beta \mu_B B)$   $\leftarrow$  same as classical model
  - $\hookrightarrow$  susceptibility at zero field:  $\chi|_{B=0} = \frac{M \mu_B}{k_B T} \sim \frac{1}{T} \leftarrow$  Curie's law
- At low temperatures,  $M \approx \mu_B^2 g(E_F) B$ 
  - $\hookrightarrow$  susceptibility  $\rightarrow$  constant:  $\chi = \mu_B^2 g(E_F)$
  - $\hookrightarrow$  only states near the Fermi surface can flip spins
  - $\hookrightarrow$  materials with  $\chi > 0$  are paramagnetic

# Classical Thermodynamics

## The Zeroth Law

- An **insulated** system is one that is inside **adiabatic walls**  $\rightarrow$  isolated from external influences
- A **diathermal** wall separates systems in **thermal contact**
- Equilibrium** is a state in which macroscopic variables are constant.

**Zeroth law: transitivity of equilibrium**

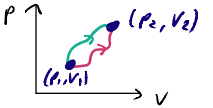
$$\begin{array}{ccc} A \xleftrightarrow{\text{eq}} C & & \\ B \xleftrightarrow{\text{eq}} C & \Rightarrow & A \xleftrightarrow{\text{eq}} B \end{array}$$

- Zeroth law defines a temperature scale:
  - $\hookrightarrow$  A, C in equilibrium  $\Rightarrow F_{AC}(p_A, V_A; p_C, V_C) = 0 \Rightarrow V_C = f_{AC}(p_A, V_A; p_C)$
  - $\hookrightarrow$  B, C in equilibrium  $\Rightarrow V_C = f_{BC}(p_B, V_B; p_C)$
  - $\hookrightarrow$  eliminate  $V_C \Rightarrow f_{AC}(p_A, V_A; p_C) = f_{BC}(p_B, V_B; p_C)$  (\*)
  - $\hookrightarrow$  zeroth law  $\Rightarrow$  A, B in equilibrium  $\Rightarrow f_{AB}(p_A, V_A; p_B, V_B)$  (†)
  - $\hookrightarrow$  (†) means that we can eliminate  $p_C$  from (\*). This means that  $\theta_A(p_A, V_A) = \theta_B(p_B, V_B)$
  - $\hookrightarrow$   $\theta(p, V)$  is the **temperature**,  $T = \theta(p, V)$  is the **equation of state**.

## The First Law

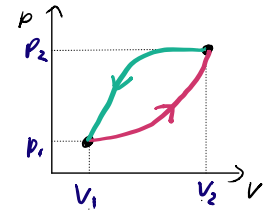
- First law**: amount of work required to change an isolated system from state 1  $\rightarrow$  2 is independent of how the work is performed
- There is some function of state  $E(p, V) \rightarrow$  **energy**, such that  $\Delta E = W$
- A non-isolated system may also gain energy via **heat transfer**

- 1<sup>st</sup> law is **conservation of energy**:  $\Delta E = Q + W$
- A **quasi-static** process is one for which the sys. is always in equilibrium (though the 1<sup>st</sup> law can describe violent changes)
  - $\hookrightarrow$  can write 1<sup>st</sup> law infinitesimally:  $dE = dQ + dW$
  - $\hookrightarrow$  E is a func. of state so dE is a total derivative
  - $\hookrightarrow$  however, Q, W are not functions of state, so dQ, dW only mean that the quantities are small.
- For compression,  $dW = -pdV \leftarrow$  work done on system
  - $\hookrightarrow \int dE = E(p_2, V_2) - E(p_1, V_1) \leftarrow$  independent of path
  - $\hookrightarrow \int dW = - \int_{V_1}^{V_2} p dV \leftarrow$  depends on path



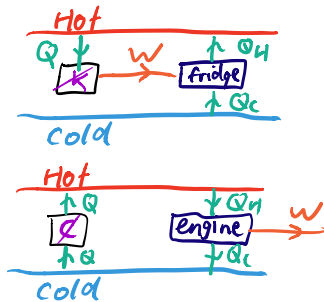
## The Second Law

- A **reversible process** is a quasi-static process that can be run backwards
- For a closed loop on a pV diagram:
  - $\hookrightarrow \oint dE = 0$  since E is a func. of state
  - $\hookrightarrow$  but  $\oint p dV \neq 0$
  - $\hookrightarrow$  1<sup>st</sup> law  $\Rightarrow \oint dQ = \oint p dV$
  - $\hookrightarrow$  i.e. reversible cycles can convert heat  $\leftrightarrow$  work



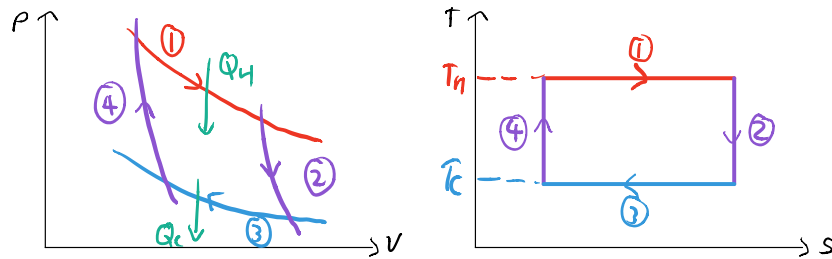
- Second law (Kelvin)**: no process is possible whose sole effect is to convert heat entirely into work.
- Second law (Clausius)**: no process is possible whose sole effect is to transfer heat from a colder to a hotter body.
- 2<sup>nd</sup> law defines an arrow of time (e.g. clausius  $\Rightarrow$  hot  $\xrightarrow{\text{heat flow}}$  cold)

- Kelvin violator  $\Rightarrow$  Clausius violator: net  $Q_H - Q = Q_C$  transferred from cold to hot
- Clausius violator  $\Rightarrow$  Kelvin violator:



### Carnot Cycle

- Reversible cycles do not violate Kelvin's 2<sup>nd</sup> law because they deposit heat.
- Carnot cycle:

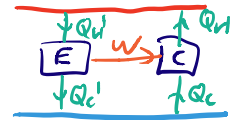


- 1 Isothermal expansion at  $T_H$ ;  $Q_H$  absorbed from hot res.
- 2 Adiabatic expansion;  $T \downarrow$
- 3 Isothermal compression at  $T_C$ ;  $Q_C$  dumped into cold res
- 4 Adiabatic compression;  $T \uparrow$

- Work done is  $W = Q_H - Q_C$  with efficiency  $\eta \equiv \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}$
- $\Rightarrow \eta = 1$  would violate Kelvin's 2<sup>nd</sup> law

- Carnot's theorem: of all the heat engines operating between two heat reservoirs, a reversible engine has the highest efficiency

$\hookrightarrow$  prove by coupling another engine to drive a Carnot pump



$\hookrightarrow$  net effect is to extract  $Q_H' - Q_H$  of heat. Clausius  $\Rightarrow Q_H' > Q_H \Rightarrow \eta_E \leq \eta_C$

- Corollary: all reversible engines have the same efficiency  $\eta(T_H, T_C)$

$\hookrightarrow$  use a Carnot engine to drive the other engine in reverse  
 $\hookrightarrow \eta_E \leq \eta_C$  and  $\eta_C \leq \eta_E \Rightarrow \eta_C = \eta_E$

- The Carnot cycle defines a thermodynamic temperature scale:

$\hookrightarrow$  let  $T_1 > T_2 > T_3$  and consider 2 Carnot engines operating between  $T_1, T_2$  and  $T_2, T_3$  respectively

$$\hookrightarrow Q_2 = Q_1(1 - \eta(T_1, T_2)) \text{ and } Q_3 = Q_2(1 - \eta(T_2, T_3))$$

$$\Rightarrow Q_3 = Q_1(1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3))$$

$\hookrightarrow$  but can also treat as one engine between  $T_1, T_3$

$$\therefore Q_3 = Q_1(1 - \eta(T_1, T_3))$$

$$\Rightarrow (1 - \eta(T_1, T_3)) = (1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3))$$

$$\Rightarrow 1 - \eta(T_1, T_2) = \frac{f(T_2)}{f(T_1)}$$

$T_2$  must cancel

$\hookrightarrow$  we can choose  $f(T) = T$

- This definition of temperature coincides with the ideal gas temp:

$\hookrightarrow$  isotherms:  $Q_H = \int_A^B p dV = \int_A^B \frac{Nk_B T}{V} dV = Nk_B T \ln\left(\frac{V_B}{V_A}\right)$

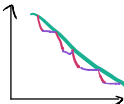
$Q_C = -Nk_B T_C \ln\left(\frac{V_D}{V_C}\right)$  similarly

$\hookrightarrow$  adiabats:  $dQ = 0 \Rightarrow dE = CvdT = -pdV \Rightarrow TV^{2/3} = \text{const}$

$$\Rightarrow V_A/V_B = V_D/V_C$$

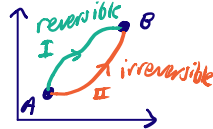
$$\hookrightarrow \eta = 1 - \frac{Q_C}{Q_H} = 1 + \frac{T_C \ln(V_D/V_A)}{T_H \ln(V_D/V_C)} = 1 - \frac{T_C}{T_H} \quad \leftarrow \text{agrees with Carnot.}$$

### Entropy of reversible processes

- For a Carnot cycle,  $Q_H/T_H = Q_C/T_C \Rightarrow \sum_i \frac{Q_i}{T_i} = 0$  ← heat absorbed
- A general path can be split into infinitesimal adiabats and isotherms. 

- For a general reversible process  $\oint \frac{dQ}{T} = 0$
- This implies  $\frac{dQ}{T}$  is path-independent  $\Rightarrow$  function of state
- Call this **entropy** (coincides with previous definition)

- For an irreversible engine  $\frac{Q_H'}{T_H} - \frac{Q_C'}{T_C} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} + \underbrace{(Q_H' - Q_H)}_{>0 \text{ because of efficiency}} \left( \frac{1}{T_H} - \frac{1}{T_C} \right) \leq 0$

- For a general irreversible path  $\oint \frac{dQ}{T} \leq 0$  (**Clausius inequality**)
- Consider paths **I** and **II**:  $\oint \frac{dQ}{T} = \int_I \frac{dQ}{T} - \int_{II} \frac{dQ}{T}$
- $\Rightarrow \int_I \frac{dQ}{T} \leq S(B) - S(A)$  
- For an isolated system  $dQ=0 \Rightarrow S(B) \geq S(A)$

### Thermodynamic potentials

- The state of a system can be specified using 2 of:

$$p \quad V \quad E \quad T \quad S$$

- each has 'natural variables', e.g.  $dE = TdS - pdV \Rightarrow E = E(S, V)$
- mixed partials give **Maxwell relations**:  $\frac{\partial^2 E}{\partial S \partial V} = \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial p}{\partial S} \right)_V$

- Can define different potentials:

- Helmholtz**:  $F = E - TS \Rightarrow dF = -SdT - pdV$
  - Gibbs**:  $G = E + pV - TS \Rightarrow dG = -SdT + Vdp$
  - Enthalpy**:  $H = E + pV \Rightarrow dH = TdS + Vdp$
- } each has a Maxwell relation

- Mnemonic: Good Physicists Have Studied Under Very Fine Teachers

- ↳ natural variables next to potential

- ↳ differential: opposite corners for coeff, then

follow diag to get differential (no sign)

- ↳ Maxwell relations:  $\begin{matrix} \text{L} & = & \text{J} \\ \text{P} & & \text{T} \end{matrix}$  and rotations

e.g.  $\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p \Rightarrow \left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p$

-S	U	V
H		F
-p	G	T

- If particle number may vary, we must add  $\mu dN$

- G is extensive  $\Rightarrow G(T, p, \lambda N) = \lambda G(T, p, N)$

$$\Rightarrow G(T, p, N) = \mu(T, p) N \quad \leftarrow \mu \text{ is Gibbs free energy per unit particle}$$

### The Third Law

- Third law**:  $\frac{S}{N} \rightarrow 0$  as  $T \rightarrow 0$  and  $N \rightarrow \infty$

- ↳ i.e. ground state entropy is not extensive

- ↳ provides an absolute reference for entropy

- Heat capacities  $\rightarrow 0$  as  $T \rightarrow 0$  since  $S(B) - S(A) = \int_A^B dT \frac{C_V}{T}$

- ↳ classical ideal gases violate this

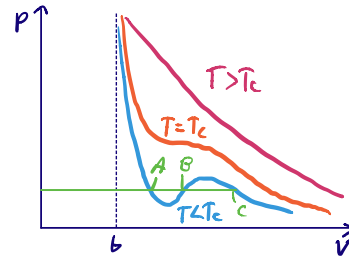
- ↳ low temperatures need QM

# Phase Transitions

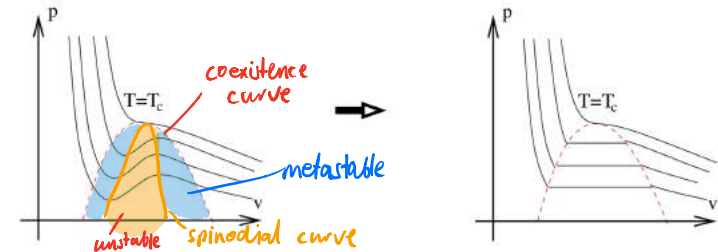
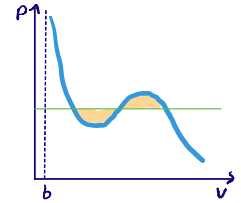
A **phase transition** is a discontinuous change in system properties

## Liquid-Gas transition

- van der Waals equation:  $p = \frac{K_0 T}{v-b} - \frac{a}{v^2}$ , using  $v = \frac{V}{N}$ 
  - ↳ shape of isotherm depends on temperature
  - ↳ at high  $T$ , ignore  $\frac{a}{v^2} \rightarrow$  monotonically decreasing
  - ↳ at  $T=T_c$ , there is a saddle point  
 $\frac{\partial p}{\partial v} = 0, \frac{\partial^2 p}{\partial v^2} = 0 \Rightarrow K_0 T_c = \frac{8a}{27b}$
- For  $T < T_c$ , a given pressure can correspond to several densities
  - ↳ solution  $B$  is unstable because  $(\frac{\partial p}{\partial v})_T > 0$
  - ↳ solution  $A$  has closely-packed and is hard to compress since  $|\frac{\partial p}{\partial v}|$  is large  $\rightarrow$  this is a **liquid**
- Two phases are in equilibrium when:
  1. Same temp. } satisfied for A, B, C since on isotherm
  2. Same pressure }
  3. Same chemical potential, i.e.  $\mu_{\text{liquid}} = \mu_{\text{gas}}$
- Equilibrium only depends on intensive quantities, so we can scale up  $N_{\text{liquid}}$  and  $N_{\text{gas}}$ .



- To solve  $\mu_{\text{liquid}} = \mu_{\text{gas}}$ , vary  $\mu(p, T)$  along an isotherm
  - ↳  $d\mu = \left(\frac{\partial \mu}{\partial p}\right)_T dp$ .  $G(p, T, N) = \mu(p, T)N \Rightarrow \left(\frac{\partial \mu}{\partial p}\right)_T = \frac{1}{N} \left(\frac{\partial G}{\partial p}\right)_{T, N}$
  - ↳ starting at  $\mu_{\text{liquid}}$  and integrating,  $\mu(p, T) = \mu_{\text{liquid}} + \int_{p_{\text{liquid}}}^p dp' \frac{v(p', T)}{N}$
  - ↳ for  $\mu_{\text{liquid}} = \mu_{\text{gas}}$ , the integral must vanish
  - ↳ this is the **Maxwell construction**  $\rightarrow$  areas of shaded regions must be equal for liquid and gas to coexist
- For a fixed  $T < T_c$ , there is a unique equilibrium pressure
  - ↳ the set of all these pressures defines the **coexistence curve**
  - ↳ inside the curve, average density may vary (between the liquid and gas densities)
  - ↳ if we cool a particular system to a point inside the curve, it will undergo **phase separation**: liquid and gas coexist



- The coexistence curve encompasses the unstable regions where  $(\frac{\partial p}{\partial v})_T > 0$  but also **metastable** regions where  $(\frac{\partial p}{\partial v})_T < 0$ 
  - ↳ these states (between **spinodal** and **coexistence** curves) have higher  $G$  than the liquid-gas eq, but can be reached (**supercooling**)



## Clausius-Clapeyron equation

- On the  $p$ - $T$  plane, the co-existence curve becomes a line  $\rightarrow$  phase boundary

$\rightarrow$  crossing the boundary involves a discontinuous change in volume.

$\rightarrow$  for  $T > T_c$  there is no distinction between liquid and gas (i.e. continuous change in volume)

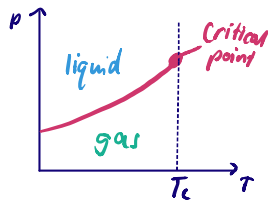
- On the phase boundary,  $g_l = g_g \Rightarrow \frac{G_l}{N_l} = \frac{G_g}{N_g}$

$$\begin{aligned} \rightarrow dG &= -SdT + Vdp \Rightarrow dg_l = -s_l dT + v_l dp \\ dg_g &= -s_g dT + v_g dp \end{aligned} \quad \left. \vphantom{\begin{aligned} dg_l \\ dg_g \end{aligned}} \right\} \begin{array}{l} \text{quantities per} \\ \text{particle} \end{array}$$

$\rightarrow$  setting  $dg_l = dg_g$ , we get an expression for the slope of the phase boundary:  $\frac{dp}{dT} = \frac{(s_g - s_l)}{(v_g - v_l)}$

$\rightarrow$  define the specific latent heat  $L \equiv T(s_g - s_l)$

$\rightarrow$  Clausius-Clapeyron equation:  $\frac{dp}{dT} = \frac{L}{T(v_{gas} - v_{liq})}$



- A phase transition is  $n$ th order if the  $n$ th derivative of a thermodynamic potential is discontinuous (Ehrenfest classification)

$\rightarrow$  liquid-gas is 1st order:  $(\frac{\partial F}{\partial T})_V$ ,  $(\frac{\partial G}{\partial P})_T$  are discontinuous

$\rightarrow$  as  $T \rightarrow T_c$ ,  $s_l \rightarrow s_g$  so the discontinuity diminishes (becomes a 2nd order transition)

## The Law of Corresponding States

- At the critical point,  $\frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0$ .

- Alternate derivation  $\rightarrow$  rearrange vdW into a cubic:  $pv^3 - (pb + k_B T)v^2 + av - ab = 0$

$\rightarrow$  at  $T = T_c$ , the equation goes from having 3 real roots to 1, so at  $T_c$  all 3 coincide  $\Rightarrow p_c(v - v_c)^3 = 0$   
 $\Rightarrow k_B T_c = \frac{8a}{27b}$ ,  $v_c = 3b$ ,  $p_c = \frac{a}{27b^2}$

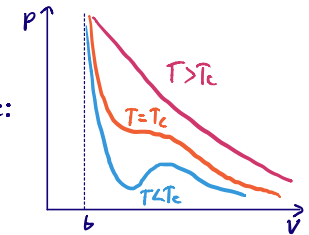
- We can rewrite the vdW equation using reduced variables  $\bar{T} = T/T_c$ ,  $\bar{V} = V/v_c$ ,  $\bar{p} = P/p_c$  and write  $a, b$  in terms of critical quantities  $\rightarrow$  should now apply to all gases.

$\rightarrow$  result is the Law of Corresponding States:  $\bar{p} = \frac{8\bar{T}}{3\bar{V} - 1} - \frac{3}{\bar{V}^2}$

$\rightarrow$  universal compressibility ratio:  $\frac{p_c v_c}{k_B T_c} = \frac{3}{8} = 0.375$

$\rightarrow$  vdW overestimates compressibilities.

- Plotted in the  $\bar{p}$ - $\bar{T}$  plane, coexistence curves of many different gases coincide  $\rightarrow$  universality.



## Critical exponents

- We can analyse how quantities vary near the critical point then compare with experiment.

① How does  $v_g - v_l$  vary along the coexistence curve as  $T \rightarrow T_c$ ?

$\rightarrow$  Law of corresponding states gives  $\bar{T}(v_{gas}, v_{liquid})$

$\rightarrow$  expand in small  $v_g - v_l$  to get  $v_g - v_l \sim (T_c - T)^{1/2}$

② How does the volume change with pressure along the critical isotherm?

↳ at  $T=T_c$ , pressure is single-valued

$$\text{↳ } \frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0 \Rightarrow p-p_c \sim (v-v_c)^3$$

③ Define the compressibility  $\kappa \equiv -\frac{1}{v} \frac{\partial v}{\partial p} \Big|_T$ . How does  $\kappa$  change as  $T \rightarrow T_c$ ?

$$\text{↳ at the critical point } \frac{\partial p}{\partial v} \Big|_{T_c} = 0 \Rightarrow \frac{\partial p}{\partial v} \Big|_{T, v_c} \sim T - T_c$$

$$\Rightarrow \kappa \sim (T - T_c)^{-1}$$

↳ so  $\kappa$  diverges as  $T \rightarrow T_c$

• Experiments do not support these results, even though we only assumed analyticity:

$$\left. \begin{array}{l} \text{① } v_g - v_l \sim (T - T_c)^\beta, \quad \beta \approx 0.32 \\ \text{② } p - p_c \sim (v - v_c)^\delta, \quad \delta \approx 4.8 \\ \text{③ } \kappa \sim (T - T_c)^{-\gamma}, \quad \gamma \approx 1.2 \end{array} \right\} \text{critical exponents}$$

• These discrepancies arise from fluctuations

↳ in grand canonical,  $\frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}}$  ← density fluctuations diminish

$$\text{↳ } \ln Z_{\text{grand}} = \beta p(T, \mu) V$$

$$\text{↳ } N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{\text{gr}} = V \frac{\partial p}{\partial \mu} \Big|_{T, \mu} \quad \text{and} \quad \Delta N^2 = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} \Big|_{T, \mu}$$

$$\Rightarrow \frac{\Delta N^2}{N} = \frac{1}{\beta V} \frac{\partial \langle N \rangle}{\partial \mu} \Big|_{T, \mu}$$

$$\text{↳ using the cyclic relation } \frac{\Delta N^2}{N} = -\frac{1}{\beta} \left( \frac{\partial \langle N \rangle}{\partial v} \right)_{p, T} \cdot \underbrace{\frac{1}{V} \left( \frac{\partial v}{\partial p} \right)_{N, T}}_{= -\kappa}$$

↳  $\kappa$  diverges as  $T \rightarrow T_c$  so fluctuations become large.

## The Ising Model

• Ising model: a  $d$ -dimensional lattice of  $N$  spins with  $s_i = \pm 1$

• Two contributions to lattice energy:

1. Interactions of spins with magnetic field

2. Interactions of neighbouring spins

$$\Rightarrow E = -J \sum_{\langle ij \rangle} s_i s_j - B \sum_i s_i$$

↳  $\langle ij \rangle$  sums over the  $q \equiv 2d$  nearest neighbours

• If  $J > 0$ , spins prefer to be aligned (ferromagnetic)

• Work in canonical ensemble ( $N$  fixed)  $\Rightarrow Z = \sum_{\{s_i\}} e^{-\beta E(\{s_i\})}$   
 ↳ magnetisation is the average spin:  $m = \frac{1}{N} \sum_i \langle s_i \rangle = \frac{1}{N\beta} \frac{\partial \ln Z}{\partial B}$

• The partition func can be approximated using mean field theory for small fluctuations:

$$\text{↳ } s_i s_j = [(s_i - m) + m][(s_j - m) + m] = (s_i - m)(s_j - m) + m(s_i + s_j - 2m) + m^2$$

$$\text{↳ neglect } (s_i - m)(s_j - m) \Rightarrow E_{\text{mf}} = -J \sum_{\langle ij \rangle} [m(s_i + s_j) - m^2] - B \sum_i s_i$$

↳ there are  $Nq/2$  nearest neighbour pairs

$$\Rightarrow E_{\text{mf}} = \frac{1}{2} J N q m^2 - (J q m + B) \sum_i s_i$$

↳ this is now just a 2-state system with  $B_{\text{eff}} = B + J q m$

• With the MF approx, we have  $Z = e^{-\frac{1}{2} \beta J N q m^2} 2^N \cosh^N \beta B_{\text{eff}}$

↳ can self-consistently solve for  $m \Rightarrow m = \tanh(\beta B + \beta J q m)$

energy of configuration



• If  $B=0$ ,  $m = \tanh(\beta J q m) \rightarrow$  solve graphically

$\hookrightarrow \tanh(\beta J q m) \sim \beta J q m$  near the origin

$\hookrightarrow$  for  $\beta J q < 1$  (high temp), the only solution is  $m=0$ .

Thermal fluctuations dominate.

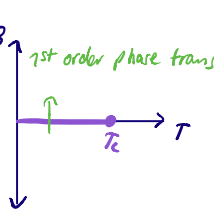
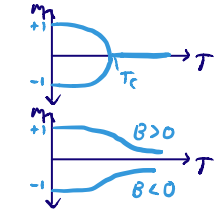
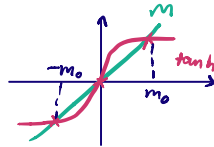
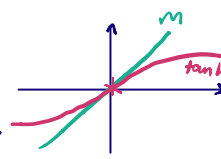
$\hookrightarrow$  if  $\beta J q > 1$ , there are 3 solutions.  $m=0$  is unstable, but  $m = \pm m_0$  are stable

$\hookrightarrow$  at some  $T = T_c$  given by  $\beta J q = 1$ , there is a discontinuous change in magnetisation

• For  $B \neq 0$ , magnetisation  $\rightarrow 0$  smoothly as  $T \rightarrow \infty$

$\hookrightarrow$  at low temperatures, the only stable solution has  $m = \text{sign}(B)$  (other 2 are unstable)

$\hookrightarrow m$  changes discontinuously if we vary  $B$ , so there is a phase boundary on the  $B$ - $T$  plane



③ How does the susceptibility  $\chi = N \left( \frac{\partial m}{\partial B} \right)_T$  vary as  $T \rightarrow T_c$  from above ( $B=0$ )?

$$\hookrightarrow \chi = \frac{N\beta}{\cosh^2(\beta J q m)} \left( 1 + \frac{J q}{N} \chi \right)$$

$$\hookrightarrow T \rightarrow T_c \Rightarrow m \rightarrow 0 \quad \therefore \chi = \frac{N\beta}{1 - J q \beta} \sim (T - T_c)^{-1}$$

$\hookrightarrow \chi$  diverges, similar to compressibility

• For  $d=1$ , MFT is completely wrong (no phase transition)

• For  $d > 2$ , MFT is qualitatively correct but quantitatively wrong.  
 $\hookrightarrow$  e.g. for  $d=2$   $m_0 \sim (T_c - T)^\beta$ ,  $\beta = 1/8$   
 $m \sim B^{1/\delta}$ ,  $\delta = 15$   
 $\chi \sim (T - T_c)^{-\gamma}$ ,  $\gamma = 7/4$

$\hookrightarrow d=3$  measured values of critical exponents are the same as for the liquid-gas system.

• For  $d > 4$ , MFT is very nearly correct.

## Critical exponents

① How does  $m$  vary as  $T \rightarrow T_c$  from below ( $B=0$ )?

$\hookrightarrow$  Taylor expansion of  $\tanh \Rightarrow m \approx \beta J q m - \frac{1}{3} (\beta J q m)^3 + \dots$

$\hookrightarrow m_0 \sim \pm (T_c - T)^{1/2} \rightarrow$  turns off abruptly when  $T = T_c$

$\hookrightarrow$  analogous to  $v_g - v_l \sim (T_c - T)^{1/2}$  for liquid-gas vdW

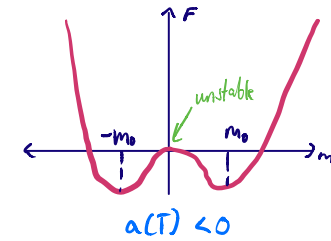
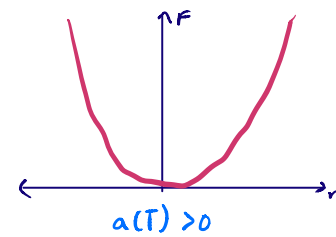
② How does  $m$  vary with  $B$  at  $T = T_c$

$\hookrightarrow \beta J q = 1 \Rightarrow m = \tanh\left(\frac{B}{J q} + m\right) \approx m + \frac{B}{J q} - \frac{1}{3} \left(m + \frac{B}{J q}\right)^3 + \dots$

$\hookrightarrow m \propto B^{1/3}$ , analogous to  $(v - v_c) \sim (p - p_c)^{1/3}$  from vdW

## Landau theory

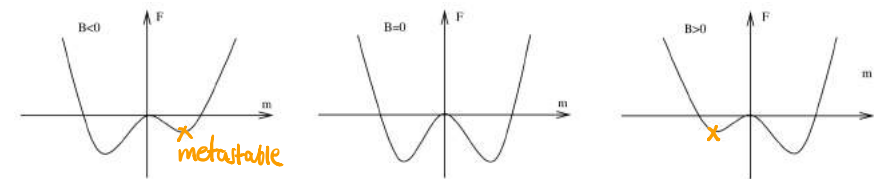
- Landau theory is a unified way of understand phase transitions (applies to all systems).
- MF approx for Ising:  $Z = e^{-\frac{1}{2}BJqNm^2} 2^N \cosh^N(\beta B_{\text{eff}})$ 
  - $\hookrightarrow F = -\frac{1}{\beta} \ln Z = \frac{1}{2} JNqm^2 - \frac{N}{\beta} \ln[2 \cosh(\beta B_{\text{eff}})]$
- $\hookrightarrow$  Landau theory considers  $F(m)$  without finding the 'correct' self-consistent value of  $m$ .
  - $\hookrightarrow$  equilibrium config:  $\frac{\partial F}{\partial m} = 0 \Rightarrow m = \tanh(\beta B_{\text{eff}})$  ← agrees with previous result
- In Landau theory,  $m$  is an **order parameter** ( $m \neq 0$  ordered,  $m = 0$  random)
  - $\hookrightarrow$  for general systems, the order parameter should be finite below  $T_c$  but vanishes above  $T_c$
  - $\hookrightarrow$  e.g for liquid-gas system, use  $m = V_{\text{gas}} - V_{\text{liquid}}$
  - $\hookrightarrow$  we can then expand the free energy in the vicinity of  $T_c$ , where  $m$  is small.
- Assume the free energy is symmetric in  $m$  (as in Ising with  $B=0$ )
  - $\hookrightarrow$  expansion:  $F(T; m) = F_0(T) + a(T)m^2 + b(T)m^4 + \dots$
  - $\hookrightarrow$  assume  $b(T) > 0$  (such that  $F \uparrow$  for large  $m$ ), so equilibrium behaviour depends on the sign of  $a(T)$
  - $\hookrightarrow a(T_c) \equiv 0$ , so as  $T$  decreases, we go from  $a(T) > 0 \rightarrow a(T) < 0$



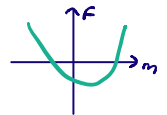
- $\hookrightarrow$  can be shown that this is a 2<sup>nd</sup> order phase transition
- Typically  $a(T) \approx a_0(T - T_c)$  and  $b(T) = b_0$ 
  - $\hookrightarrow \frac{\partial F}{\partial m} = 0 \Rightarrow m_0 = \sqrt{\frac{a_0}{2b_0}} (T_c - T)^{1/2}$  for  $T < T_c$
  - $\hookrightarrow$  this reproduces the critical exponent of the Ising/vdW systems

## 1<sup>st</sup> order phase transition

- Now we allow asymmetry in  $m$ , e.g  $B \neq 0$  Ising model.
 
$$F(T; m) = F_0(T) + \alpha(T)m + a(T)m^2 + \gamma(T)m^3 + b(T)m^4 + \dots$$
  - $\hookrightarrow$  as before, assume  $b(T) > 0$
  - $\hookrightarrow$  as  $B$  changes from +ve to -ve,  $\alpha$  and  $\gamma$  change sign
  - $\hookrightarrow$  for low temperatures, a nonzero field results in 1 stable equilibrium



- At high temperatures, the metastable equilibrium disappears at the spinodal point



## Landau-Ginzberg theory

- Corrects Landau theory by including fluctuations in the order param.

↳ order param becomes  $m(\underline{r})$

↳ free energy now has a 'stiffness' that resists changing  $m$

↳ free energy is now a functional, e.g. in symmetric case:

$$F[m(\underline{r})] = \int d^d r [a(T)m^2 + b(T)m^4 + c(T)(\nabla m)^2 + \dots]$$

- Minimise using the calculus of Variations

↳  $m(\underline{r}) \rightarrow m(\underline{r}) + \delta m(\underline{r})$

$$\begin{aligned} \delta F &= \int d^d r [2a m \delta m + 4b m^3 \delta m + 2c (\nabla m) \cdot \nabla \delta m + \dots] \\ &= \int d^d r [2a m + 4b m^3 - 2c \nabla^2 m + \dots] \delta m \end{aligned}$$

$$\delta F = 0 \Rightarrow c \nabla^2 m = a m + 2b m^3$$

↳  $m = \text{const}$  recovers Landau theory

↳ in 1D, Landau-Ginzberg theory describes domain walls.